[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

# A QUANTITATIVE STUDY OF THE REACTION BETWEEN DISUBSTITUTED ACETYLENIC HYDROCARBONS AND THE GRIGNARD REAGENT

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In connection with studies on the mechanism of reaction between the Grignard reagent and compounds having more than one reactive group it was shown previously[1] that ethylmagnesium iodide does not add to several typical ethylenic hydrocarbons under various conditions. A similar quantitative study has been made with disubstituted acetylenic hydrocarbons.

Acetylene and monosubstituted acetylenic compounds, such as phenylacetylene, having so-called active or acidic hydrogens, undergo ready reaction with RMgX compounds, as a result of which the hydrogens are replaced by —MgX groups. These acetylenemagnesium halides (RC≡CMgX) have been shown by Yocich[2] and many others to give virtually all of the reactions of RMgX compounds. However, there appears to be no definitely established case of addition of the Grignard reagent to the acetylenic linkage. Blaise,[3] in a qualitative investigation, attempted to bring about a reaction between the Grignard reagent and phenylacetylene, but was unsuccessful. The work of Kohler[4] and the later studies of others on the interaction of the Grignard reagent and unsaturated carbon compounds indicate an apparent addition to the ethylenic linkage. In all of these cases, however, we are dealing with 1,4-addition and the apparent addition to the *ethylenic* linkage is due to the rearrangement of the enol that results when the addition compound is hydrolyzed. It is significant that Wilson and Hyslop,[5] in a recent study with some corresponding conjugated systems having an acetylenic linkage, did not get a related apparent addition to the *acetylenic* linkage.

The method employed in the present work is essentially identical with that used by Gilman and Crawford[1] in the quantitative study with ethylenic hydrocarbons. It is shown that the Grignard reagent does not add to an acetylenic linkage.

The compounds studied were ethyl-phenyl-acetylene ($C_6H_5C{\equiv}CC_2H_5$), tolane ($C_6H_5C{\equiv}CC_6H_5$) and diphenyl-diacetylene ($C_6H_5C{\equiv}C{-}C{\equiv}CC_6H_5$). The last was selected because of its conjugated system of acetylenic linkages. In addition, the results include a study of di-*p*-tolyl-

[1] Gilman and Crawford, THIS JOURNAL, **45**, 554 (1923).

[2] Yocich, *J. Russ. Phys.-Chem. Soc.*, **38**, 1040 (1906); *C. A.*, **1**, 1271 (1907).

[3] Blaise, *Compt. rend.*, **132**, 38 (1901).

[4] Kohler and others, *Am. Chem. J.*, **31**, 642 (1904), etc.

[5] Wilson and Hyslop, *J. Chem. Soc.*, **123**, 2612 (1923).

dithio-acetylene[6] ($CH_3C_6H_4SC{\equiv}CSC_6H_4CH_3$) taken from an investigation concerned with the polarity of unsaturated groups.

Ethyl-phenyl-acetylene was refluxed for 30 minutes with sufficient ethylmagnesium bromide to react with all of it. The average corrected volume of ethane liberated after hydrolysis of the reaction mixture was 158.7 cc. The corresponding volume obtained from the same aliquot portion of standard ethylmagnesium bromide after a like period of refluxing without an acetylenic hydrocarbon was 165.4 cc.

Tolane and diphenyl-diacetylene after refluxing with ethylmagnesium iodide gave as averages, 208.1 cc. and 208.7 cc. of ethane, respectively. The same aliquots of standard ethylmagnesium iodide gave an average of 218.9 cc. of ethane. Di-*p*-tolyl-dithio-acetylene and ethylmagnesium bromide gave 143.1 cc. of ethane, whereas the corresponding standard solution of ethylmagnesium bromide gave 146.8 cc. of ethane.

The differences between the volumes of ethane theoretically required if no reaction occurred and those obtained after refluxing with the acetylenic compounds are really 1.6 cc. less than those given above. This was determined by running "blank" experiments with the ethylmagnesium halides and a volume of dry ether corresponding with that used in the actual runs with acetylenic hydrocarbons. The error is very likely due to the decidedly small but equally significant amount of moisture contained in the supposedly dry pipet.

Considering other minor errors involved in a study of such active Grignard reagents, it may be said that no addition takes place.

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## Summary

It is shown that ethylmagnesium bromide and ethylmagnesium iodide do not add to several typical disubstituted acetylenic hydrocarbons.

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[6] Prepared according to the method of Fromm and Siebert, *Ber.*, **55**, 1014 (1922).